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Development of High-Temperature Batteries for Use in Geothermal and Oil/Gas Boreholes

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ABSTRACT

The drilling industry continues to drill deeper and hotter wells to support fossil fuel exploration, production and geothermal power production. Natural gas well temperatures in excess of 185°C are becoming increasingly common and geothermal power production wells can reach 350°C. Electronics manufacturers are developing new high-temperature electronic devices capable of operating at 225°C for five years. Most of these components continue to operate up to 300°C. This paper discusses efforts to develop high-temperature batteries to meet the power needs of new high-temperature electronic systems.

Background

Drilling a well or logging a well at 20,000 ft. is not too different than going to the moon. The logging and drilling tools require electronics, which operate with a high degree of reliability while at elevated temperatures. A failure of electronic devices, batteries, seals, or mechanical systems or housings can result in a significant cost to the well owner or operator. Loss of an Measurement While Drilling (MWD) tool could cost the drilling project hundreds of thousands of dollars.

Because of this risk, service companies are being pushed to develop more robust and reliable drilling and logging tools that can withstand both high pressures and high temperatures. The electronics components industry is responding with new silicon-on-insulator (SOI) devices capable of operating at 225°C for five years. Most of these components continue to operate up to 300°C. This implies that there is an existing electronic component solution for elevated temperatures. Unfortunately, there is currently no off-the-shelf solution for the battery problem for these elevated temperatures [Hensley, *et al.*, 1998]. The upper limitation of commercially available lithium thionyl chloride batteries is 200°C. There is a need for batteries that will function well above this temperature.

Sandia Battery Program Goal

The Sandia program goal is to develop a hybrid battery solution for logging and drilling tools operating between room temperature and 300°C (see Fig. 1). The hybrid battery will use a thermal battery for power and a solid-state battery for keeping the electronic memory and microprocessor alive while at room temperatures.

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Technical Introduction

A number of halide-electrolyte systems are being developed for use with the $Li(Si)/FeS_2$ and $Li(Si)/CoS_2$ couples that are used in thermally activated ("thermal") batteries. The batteries are inert until the electrolyte becomes molten. By changing the composition of the electrolyte, the electrical conductivity and thermal operating window can be varied over a wide range for the different requirements of the various applications [Guidotti and Reinhardt, 1988, Guidotti and Reinhardt, 1995, Guidotti, 1995]. Thermal batteries typically operate over an internal temperature range of 350° to 600°C. Sandia initially examined various halide compositions with the aim of lowering the operating temperature range to make such a system suitable for use in a geothermal borehole, where temperatures can be 300°C or more. The goal was to eliminate the expensive dewar and internal pyrotechnic and use the heat of the borehole to maintain the electrolyte in the molten state [Normann and Guidotti, 1996]. Modeling efforts showed such an approach had promise under certain conditions [Guidotti and Dobranich, 1996]. The use of an internally powered heater was also examined but was found impractical due to the high power requirements.

Other non-halide molten salts were also examined during the course of the study, with the major emphasis on eutectic molten nitrates. Several so-called room-temperature molten salts were evaluated for possible borehole use. In addition, screening studies of a number of organic electrolytes were performed to determine their suitability for use in the liquid state at elevated temperatures in potential borehole applications. More recently, the use of ionically conducting solid electrolytes was reevaluated for a low-current so-called "keep-alive" application for memory retention in wellbore logging tools.

Experimental

Materials Preparation and Characterization

The candidate halide- and nitrate-eutectic electrolytes were prepared by fusion of the appropriate amounts of vacuum-dried, reagent-grade ingredients. The separator materials were made by fusion of the electrolytes with 25% to 35% MgO (Merck Maglite 'S'). After grinding, the various powders were pressed into pellets. The pyrite cathode pellets were prepared from 75% acid-purified FeS_2, 25% separator, and 1.5% Li_2O. The anode pellets were similarly pressed from 44% Li/56% Si and 25% electrolyte.

The cathode pellets with the nitrate eutectic contained Ag_2CrO_4, 20% electrolyte, and 10% graphite (Lonza KS-6). The anodes were pressed from 20%Li/80%-Al or 44% Li.56% Si materials and contained 20% and 25% electrolyte, respectively.

Liquid organic electrolytes that were screened were based on propylene carbonate (PC). In some cases, ethylene carbonate (EC) was added (1:1 w/w) to improve the high-temperature stability. A number of supporting electrolytes were evaluated, including LiBr and $LiBF_4$.

Single-Cell Testing

Single cells were discharged in the glovebox under constant current load at a temperature of 200° – 500°C between heated platens at a constant applied pressure of 55.2 kPa. The cell discharge was terminated when the voltage dropped below 1.00 v.

Results and Discussion

Molten Bromide Salts

In geothermal applications, the borehole temperatures can reach 350°C. There are a number of halide-based systems that have melting points under 350°C. One electrolyte is the LiBr-KBr-LiF eutectic that melts at 324.5°C [Redey and Guidotti, 1996]. This electrolyte has the composition 57.33% LiBr-42.0% KBr-0.67% LiF. (All compositions are reported as weight percentage.) At 400°C under a steady-state load of 63 mA/cm^2, the bulk of the Li(Si)/FeS_2 cell polarization was ohmic and cathode related. The performance of the LiBr-KBr-LiF eutectic decreased dramatically at lower temperatures. When the temperature was lowered to 350°C from 400°C, the run time at a current density of 63 mA/cm^2 dropped by a factor of four to only 600 s (1-g cathode and 0.9-g anode).

To improve the lower-temperature performance, a similar eutectic electrolyte with the composition 42.75% CsBr-39.08% LiBr-18.17% KBr and a melting point of 228.5°C [Guidotti and Reinhardt, 1998] was examined. This electrolyte has operating temperatures of 300° and 250°C, the lifetimes showed similar declines with temperature for the same mass of anode and cathode, dropping from 80 s at 300°C to only 20 s at 250°C. The conductivity of the CsBr-LiBr-KBr-based separator is only about ¼ of that of the LiBr-KBr-LiF-based separator, which is the main reason for the higher impedance in the former case. The current density that can be sustained is critically dependent on the temperature and electrolyte composition.

Molten Iodide Salts

The use of iodide-based halide eutectics was next examined, as they are known to form lower-melting eutectics than the corresponding bromide or chloride analogs. There are several quaternaries based on LiI-LiBr-LiCl-LiF and melt between 325.4° and 326.1°C [Guidotti and Reinhardt, 2002].

A pentanary iodide-based electrolyte that melts at 151°C was examined. It has the composition 45.09% LiI-32.07% CsI-16.75% KI-5.14% KBr-0.95% LiCl. The initial results of single-cell tests at 200°C and 8 mA/cm^2 with the Li(Si)/FeS_2 couple were promising, in that the performance under these conditions was superior to that observed at a higher temperature of 240°C for the Li(Si)/CsBr-LiBr-KBr/FeS_2 couple at the same current density. Follow-on tests with much larger anodes and cathodes (~5 g) in two 5-cell parallel stacks at total current density of 3.8 mA/cm^2 resulted in a battery run time of 37 h before loss of the internal electrical connection occurred. (See Fig. 2.)

Problems with air oxidation of the iodide and poor repeatability forced the discontinuation of further work with this system.

Molten Nitrate Salts

Low-melting nitrate eutectics appear usable for borehole use. One nitrate eutectic has the composition 66.79% KNO_3-33.21% $LiNO_3$ and melts at 124.5°C. This electrolyte has been examined previously for possible use in reserve thermal batteries by Giwa [Giwa, 1992, Giwa 1991]. The basic electrochemistry of nitrate-containing molten-salt systems has also been studied by Miles and co-workers [Miles, 2000]. The work reported here used the Li(Al)/Ag_2CrO_4 couple.

The active reducing anodes are stable in contact with the molten oxidizing nitrates only because of the formation of a passivation layer of Li_2O. We targeted a conservative working temperature range of 150° to 300°C for possible borehole use. The performance of Li(Al)/KNO_3-$LiNO_3$/Ag_2CrO_4 single cells for these temperature ranges have a discharge current density of 7.8 mA/cm^2. The discharge time increased at 200°C relative to 150°C. However, at 250°C, the cell lifetime dropped. At 300°C, the performance dropped to below what was observed at 150°C. This behavior is believed to be due to self-discharge reactions that become increasingly more important at the higher temperatures. Apparently, the passivation layer on the Li(Al) anode becomes less protective under these conditions.

The mass (thickness) of the anode and cathode pellets had a dramatic impact on the electrochemical performance. When the thickness was increased by a factor of five, <50% of this capacity was realized. This indicates that there are severe mass-transport limitations of Li ions through such thick electrodes.

The results of the single-cell tests are promising enough that tests are underway with multiple 5-cell battery stacks connected electrically in parallel to boost the current output to obtain about 60 mA at 12 – 15 V. This arrangement would be adequate for many oil/gas borehole applications for powering the electronics drilling package.

Room-Temperature Molten Salts
The use of an electrolyte that is liquid at room temperature and thermally stable to 300°C or higher appears to offer the most promise for an ideal power source for oil/gas borehole applications. Paired with an appropriate electrochemical couple, such a system would be usable at ambient conditions as well as at the elevated temperatures in the borehole. The essential feature for the success of this approach will be a suitable room temperature molten salt (RTMS) that is chemically stable with the anode and cathode materials. One candidate RTMS that was explored was 3-ethyl-1-methylimidazolium tetrafluoroborate ($EMIBF_4$).

The chemical compatibility tests of the $EMIBF_4$ with Li(Si) and Li(Al) alloy and with Ca-metal at temperatures of 100°C, 150°C, and 200°C over a period of several weeks showed changes in color or melting point [Dunstan, *et al.*, 2002]. The $EMIBF_4$ was found to react significantly with the Li(Al) and the Li(Si) alloys at 150°C in less than an hour, with the extent of reaction with Ca being considerably less.

Tests are underway with a modified imidazolium derivative that has been coupled to an imide [$N(CF_3SO_2)_2^{-1}$] anion. Initial tests indicate that this material is thermally stable alone over 400°C. Anode compatibility tests are currently underway with this new imide.

Organic Electrolytes
PC has been used in Li ambient-temperature cells and has a boiling point of 240°C at 1 atm. A co-solvent also used in Li-ambient cells is ethylene carbonate (EC), which has an even higher boiling point. At temperatures of under 250°C, solutions of PC and EC might be usable, with the

proper supporting electrolyte. This option is currently being explored with solutions of PC and EC with supporting electrolytes of LiBr and $LiBF_4$, among others. The ionic conductivity at room temperature of a number of test solutions was a third or less than the 10 – 15 mS/cm typical of standard electrolytes used in Li-ambient cells (e.g., 1M $LiPF_6$ in EC/dimethyl carbonate). In general, the conductivities decreased at levels above 1M.

Single-cell tests are currently underway with the Li(Si)/FeS_2 couple in a number of the better tests solutions at temperatures of 50°, 100°, and 150°C.

Solid-State Inorganic Electrolytes

Solid-state inorganic (ceramic or glass) electrolytes offer some advantages over the various candidate liquid electrolytes for possible use in borehole power sources. The Li-ion conductors can be used from room temperature to well over 300°C in many cases. This is especially true for the ceramic types. Recently, a patent has been issued for a cell based on the La/BiF_3 couple and a fluoride-ion conductor [Potanin and Vedeneev, 2002]. Being usable over the entire operating temperature range envisioned for borehole power supplies offers a real advantage, in that the battery could be checked out on the surface prior to insertion into the well.

However, all of these solid ionic conductors suffer from one main disadvantage: low ionic conductivity. Their conductivities are typically several orders of magnitude lower than the liquid electrolytes. The preliminary room-temperature values for some of the glasses and glass-ceramic materials examined in the lab are listed in Table 2. These low conductivities severely limit the power available from such devices. This type of battery would be best suited for a "keep-alive" memory application, where currents would be on the order of several milliamperes or less at 3V to 5V.

Table 2. Ionic conductivity of pressed discs of some experimental and commercial glasses and glass ceramics at 25°C.

Material Composition, w/o	Ionic Conductivity, mS/cm
34.10% P_2S_5/14.49% Li_2S/51.41% LiI [Malugani, *et al.*, 1983]	0.0026
95.33% LaF_3/4.54% BaF_2/0.13% LiF [Potanin, *et al.*, 2002]	0.0038
1.83% $LiPO_4$/45.72% Li_2S/52.44% SiS_2 [Takada, *et al.*, 1996, Iwamoto, *et al.*, 1995]	0.0730
Ohara YC-LC Li-ion conductivity glass/ceramic	0.0470

Future Work

Current plans are to continue work with two hybrid batteries to cover the complete operating range from room temperature to 300°C. Both hybrids will use a solid-state battery to function as a keep-alive battery supporting the memory and microprocessor functions. The main power will come from a thermal battery after the tool has reached ambient wellbore temperatures sufficient to activate the battery. As this implies, high-temperature logging and drilling tools will have limited functionality at temperatures below the operating temperature of the thermal battery.

For most oil and natural gas wells, an operating temperature of 225°C is sufficient. A hybrid using a KNO_3-$LiNO_3$ eutectic will be the first to be tested in actual wellbore conditions.

For most geothermal wells, an operating temperature of 300°C is sufficient. A hybrid using CsBr-LiBr-KBr eutectic melting at 228.5°C seems the most likely candidate for further study. There is hope for success here for two reasons. First, the higher melting eutectic has proven to be robust in laboratory testing. Second, geothermal production wells are uniformly hot from the surface to the bottom hole. This means the geothermal battery and electronics will start operating almost immediately upon entering the well.

Conclusions

A number of molten-halide systems were examined for possible use as electrolytes for borehole power supplies. A system based on the CsBr-LiBr-KBr eutectic that melts at 228.5°C would be usable at temperatures as low as 250°C with the Li(Si)/FeS_2 couple at current densities as high as 16 mA/cm^2.

To date, no thermal battery has demonstrated acceptable reliability at temperatures between 165° and 250°C. Work is still ongoing here to gain coverage between these temperatures.

The KNO_3-$LiNO_3$ eutectic that melts at 124.5°C shows considerable promise for temperatures as low as 150°C for possible use in a borehole power source based on the Li(Al)/Ag_2CrO_4 couple. This system should be able to function at 4 – 8 mA/cm^2 over a temperature range of 150° – 250°C. However, issues of self discharge—especially under open-circuit conditions—and rechargeability still need to be addressed.

Organic electrolytes based on PC and EC with certain Li salts also show promise, but more work remains to determine the long-term stability with high-activity anodes (e.g., Li(Si)) at temperatures over 150°C.

Solid Li^+ and F^- conducting electrolytes show the greatest promise for use in "keep-alive" batteries for memory retention in the drilling tool. Because of their very high resistivities, separators based on them must be fabricated in very thin films to minimize ohmic losses.

References

Dunstan, D. J., Caja, J. and Guidotti, R. A., May 13-16, 2002, "Investigation of the Stability of Low-Temperature Ionic Liquids with High-Activity Anodes," 201st ECS Meeting, Philadelphia, PA.

Giwa, C. O., June 22, 1992, "Feasibility Study of Sulphone-Based Electrolytes for a Medium-Temperature Reserve Cell Concept," Power Sources Symposium, IEEE International Meeting, p. 215-218.

Giwa, C. O., 1991, "Feasibility Study of Materials for a Medium-Temperature Reserve Cell Concept," Materials Science Forum, Vol. 73-75, p. 699-706 [note: books is also known as Molten Salt Chemistry and Technology—NKS].

Guidotti, R. A. and Reinhardt, F. W., 1988, Evaluation of Alternate Electrolytes for use in Li(Si)/FeS2 Thermal Batteries, International Power Sources Symposium, 33rd, Cherry Hill, NJ, June 13-16, 1998, Proceedings.

Guidotti, R. A. and Reinhardt, F.W. April 24-26, 1995, Electrolyte Effects in Li(Si)/FeS(sub 2), Thermal Batteries, Conference: 19th International Power Sources Symposium, p. 443-453.

Guidotti, R. A., October 9-12, 1995, Thermal Batteries: A Technology Review and Future Directions, R.A. Conference: 27th SAMPE International Technical Conference, p. 807-818.

Guidotti, R. A. and Dobranich, D., 1996, "Potential Power Sources for High-Temperature Geothermal Applications," Transactions of the 3rd International High Temperature Electronics Conference, v. 2, p. 167-172.

Guidotti, R. A. and Reinhardt, F.W., 1998, Characterization of Low-Melting Electrolytes for Potential Geothermal Borehole Power Supplies: The LiBr-KBr-LiF Eutectic, Conference: Molten Salts-International Symposium, 11th (Molten Salts XI) Proceedings-Electrochemical Society PV, no. 11, p. 316-324.

Guidotti, R. A. and Reinhardt, F. W., May 13-16, 2002, "All-Lithium, Iodide-Based, Low-Melting Electrolytes for High-Temperature Batteries," 201st ECS Meeting, Philadelphia, PA.

Hensley, D., Milewits, M., and Zhang, Wenlin, Autumn 1998, "The Evolution of Oilfield Batteries," Oilfield Review, p. 42-57

Iwamoto, K., Aotani, N., Takada, K., and Kondo, S., 1995, Application of Li(sub 3)-Li(sub 2) Glass to the Solid State Secondary Batteries, Journal: Solid State Ionics, v. 79, p. 288-291.

Malugani, J. P., Fahys, B., Mercier, R., Robert, G., Duchange, J. P., Baudry, S., Broussely, M., and JP. Gabano, 1983, De Nouveaux Verres Conducteurs Par L'ion Lithium Et Leurs Applications Dans Des Generateurs Electrochimiques (New Lithium-ion Conducting Glasses and Their Applications in Electrochemical Generators), Journal: Solid State Ionics, Diffusion & Reactions, v. 9-10, p. 659-665.

Miles, M. H., 2000, Lithium Thermal Batteries Using Molten Nitrate Electrolytes, Power Sources Conference - 39th Proceedings of the Power Sources Conference, p. 560-563.

Normann, R. A. and Guidotti, R. A., 1996, A Study of the Use of High Temperature Electronics and Batteries to Avoid the Use of Dewars for Geothermal Logging, Geothermal Resources Council Annual Meeting, Geothermal Resources Council *Transactions,* v. 20, p. 509.

Potanin, A. A. and Vedeneev, N. I., April 30, 2002, U.S. Patent 6,379,841.

Redey, L. and Guidotti, R. A., 1996, Reevaluation of the Eutectic Region of the LiBr-KBr-LiF System, 37th Power Sources Conference, PB Reports, PB96-191556, p. 255-258.

Takada, K., Aotani, N., Iwamoto, K., and Kondo, S., 1996, Solid State Lithium Battery With Oxysulfide Glass, Solid State Ionics, v. 86-88, Part 2, p. 877-882.

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List of Figure Legends

Fig. 1. Example battery pack. Most thermal batteries are produced already fully enclosed within a steel housing. The proposed hybrid battery will look very much the same with multiple wire or thermals for power connection.

Fig. 2. Discharge characteristics of Li(Si)/LiI-CsI-KI-KBr-LiCl (MgO)/FeS_2 battery made up of two 5-cell parallel stacks and discharged at 3.8 mA/cm^2 total current density at 200°C.

Fig. 1

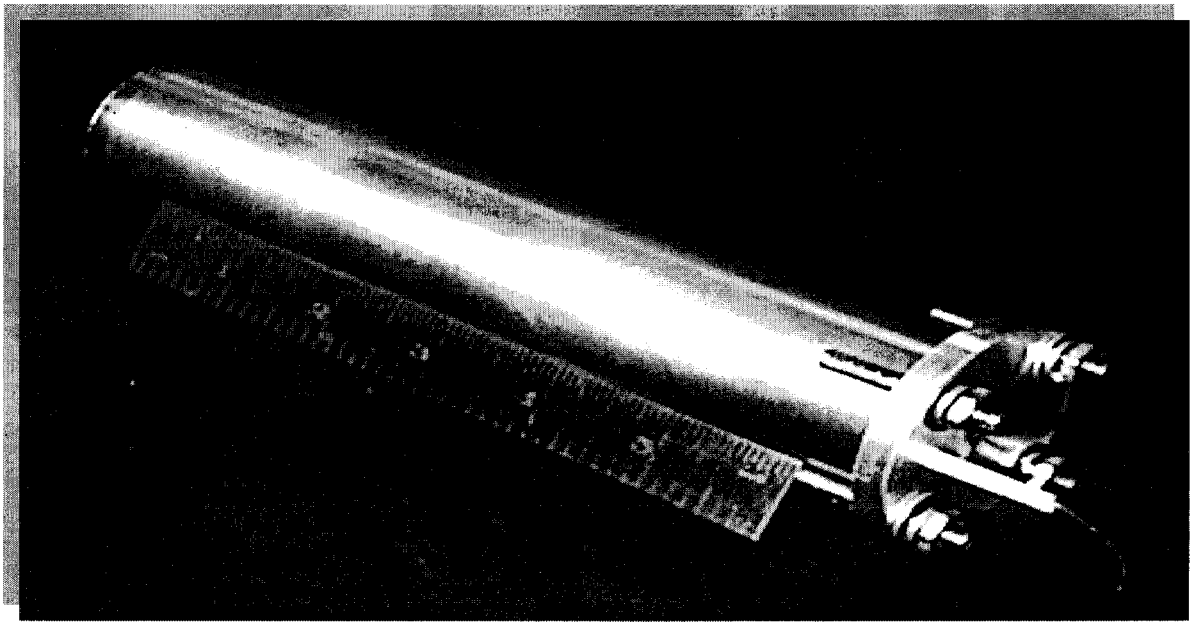
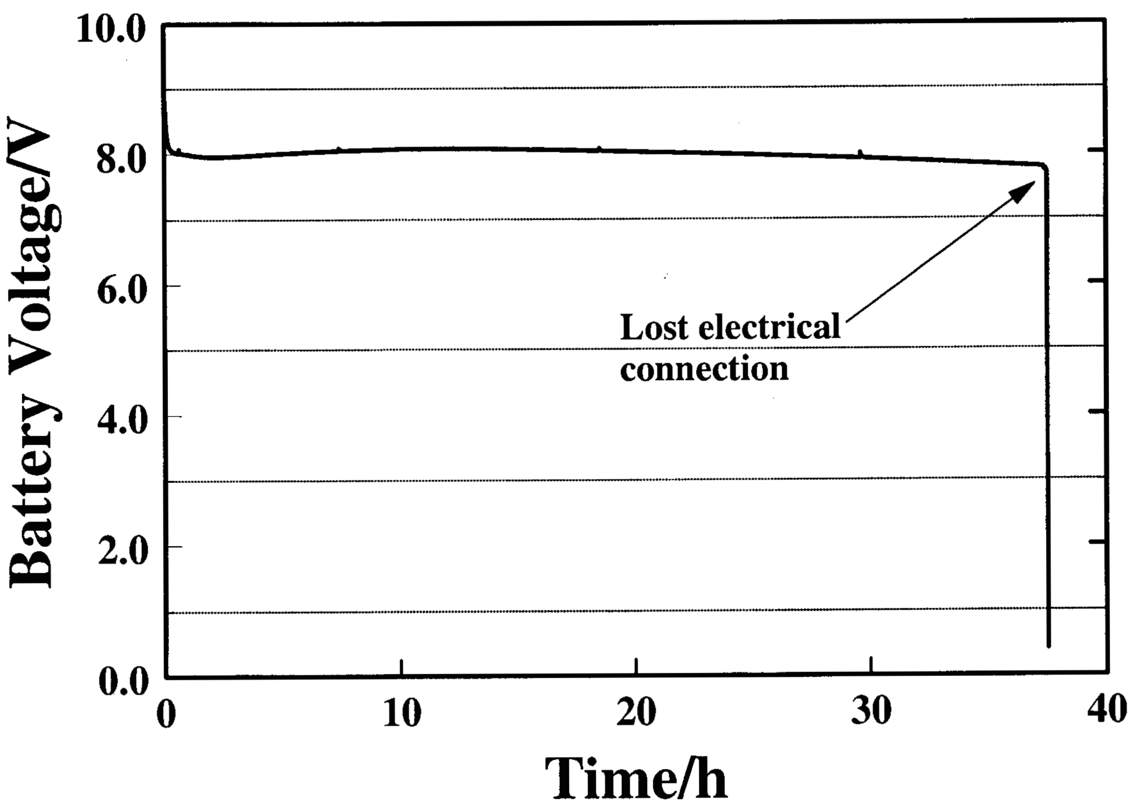


Fig. 2


10.0
8.0
6.0
4.0
2.0
0.0
0
10
20
30
40
Battery Voltage/V
Time/h
Lost electrical
connection